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OPTICAL AND PHOTOLUMINESCENT STUDIES ON VO^{2+} DOPED SnO_2 THIN FILMS

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ABSTRACT
VO^{2+} doped SnO_2 thin films have been prepared on ultra-clean glass substrates by chemical spray pyrolysis technique. UV-vis, PL, Electrical conductivity and chromaticity studies were investigated on VO^{2+} doped SnO_2 thin films. Optical absorption spectrum showed three bands at 753, 720 and 610 nm in the wavelength range 300-800 nm. DC electrical conductivity studies revealed that large value of thermoelectric power of VO^{2+} doped SnO_2thin films possess semiconductor behaviour. The thermo emf of VO^{2+} doped SnO_2thin films was studied in the temperature range 275 - 325 K using thermal probe method. Photoluminescence spectrum showed that the optical bands lie at 352 and 436 nm. The CIE (x, y)chromaticity is calculated from the emission spectrum and the coordinates were found for VO^{2+} doped SnO_2 thin films at (x = 0.2993, y = 0.4912) showed in blue and yellow regions.
Keywords: SnO_2, Chemical spray pyrolysis, Optical, dc conductivity, Thermo emf and PL studies.

INTRODUCTION

In the present scenario a significant interest has been taken place in the development and improvement of functional properties of thin films[1]. Oxide thin films are widely used in electronic devices for information processing by replacing the magnetic layers and tunnel barriers. Semiconductor metal oxides, because of their effective role as detecting devices are studied elaborately and these oxides in thin film form have wide range of applications such as flat panel display and electrochromic devices, transparent resistive heaters, anti-reflecting and gas sensors.Various approaches have been applied to fabricate thin films[2] such as chemical vapour deposition[3], RF sputtering[4], DC magnetron, spin coating[5], pulsed laser deposition[6], chemical bath deposition[7], co-precipitation[8], spray pyrolysis[9] and electrodeposition[10] at room temperature. Spray pyrolysis technique is the best approach to deposit thin films with cost effective and easy control productions on large scale. The development goes with the explosion of scientific and technological breakthrough in microelectronics, optoelectronics and nanotechnology[11]. In the 21st century an attractive attention has been made by the researchers towards transition metal oxides due to their excellent physical and chemical properties, in order to promote these materials for LEDs, electroluminescent panels and plasma display devices. Among all the transition metal ions, tin oxide (SnO_2) is a promising candidate in the field of catalysis, photograph, electronics, photonics, data storage, optoelectronics etc. Moreover tin oxide thin films have many merits, such as non toxic, wide band gap(3.4-3.6 eV), excellent optical transparency with n-type semiconducting nature[12].The main drawback of SnO_2 thin films is to control oxygen at deposition process, due to non-stoichiometric nature of oxygen; SnO_2 converts the metastable phases as SnO or Sn_3O_4 and conduction phenomenon takes place in SnO_2 thin films due to random distribution of electrons[13,14].

Vanadium (V) is a natural abundance element which is freely available from earth crust. The atomic number of vanadium is 23 and it pocesses silvery-grey colour. The chemistry of the coordination compounds of vanadium is largely dominated by that of the vanadyl ion VO^{2+}, one of the simplest oxy-

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cations because of its unusually high stability. VO^{2+} entity has a discrete existence in compounds in the solid state, in the fused state, in solution and in the vapor state. VO^{2+} ion consists of a V^{4+} ion ($3d^1$ configuration) and an O^{2-} ion ($2P^6$ configuration) giving it some important similarities (viathe "hole" formalism) to the Cu^{2+} (d^9) system. Vanadium pentoxide/Vanadyl chlorides and related phases are important in catalysis. Vanadium oxide/Vanadyl chlorides are used commercially in the reduction of NO_x to N_2 by ammonia or hydrocarbons in the presence of oxygen. Rao et al. published their results on different materials in the earlier studies[15-61].

The aim of the present work is to develop and characterize thin films with improved physical, electrical and testing on lab scale with cost effective by chemical spray pyrolysis technique. In the present investigation, VO^{2+} doped (0.01 mol %) SnO_2 thin films were prepared by chemical spray pyrolysis method. Different spectroscopic techniques have been performed by UV-vis, dc conductivity, PL and chromaticity studies, to collect the information of the prepared thin films.

EXPERIMENTAL

Materials and Synthesis: Tin oxide (SnO_2) and vanadium pentoxide (V_2O_5) were purchased from sigma Aldrich Ltd., India with 98 % purity. These chemicals were used to fabricate thin films of VO^{2+} doped SnO_2 by spray pyrolysis. Initially 0.1 M aqueous solution of SnO_2 is taken in a 100 ml beaker with constant stirring, later (0.01 mol %) of V_2O_5 is gently added to prepare spray solution. The solution was placed on the hot metal surface maintained at temperature of 673 K using filtered air as carrier gas at a flow rate normalized to approximately (1.8) ml/min. The nozzle of the spray gun is dipped in the chemical solution, later the solution was sprayed on the glass substrate for 10 s with 15 s intervals. Finally the thin films were deposited on to micro-glass slides.

Characterization: Optical absorption was carried-out for the prepared thin films by JASCO V-670 Spectrophotometer in the wavelength range 500-800 nm. The dc conductivity was measured using four probe method. The thermo emf of VO^{2+} doped SnO_2thin films was studied in the temperature range 275 - 325 K using thermal probe method. Photoluminescence studies were performed at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources.

RESULTS AND DISCUSSION

Optical absorption Studies

UV-visible spectroscopy is a versatile tool which is used for the identification of intra molecular vibrations in a given sample. Optical analysis is used to identify the optical bandgap of the materials in the transmitting radiation. In an energy level a photon is absorbed, when atoms or molecules interact with incident light; they absorb energy and are transferred to higher energy states. Transition takes place in bandgap energy as it rises in the absorption process called absorption edge from where the optical bandgap energies are determined. Optical absorption spectra of VO^{2+} doped SnO_2 thin films were performed by using JASCO V-670 Spectrophotometer in the wavelength region 500-800 nm at room temperature. Three bands of absorbance peaks are formed at 610, 720 and 753 nm for prepared thin films which are clearly shown in Figure-1. The absorption spectrum is obtained due to the vibration of molecules in energy levels from ground state to exited state which depend on the nature of the symmetry and the ligand complex[62,63].

The optical absorption and their transitions ofVO^{2+} doped SnO_2 thin films are assigned to $^2B_{2g} \rightarrow ^2E_g$, $^2B_{2g} \rightarrow ^2B_{1g}$and $^2B_{2g} \rightarrow ^2A_{1g}$. The values for inter electronic repulsion parameters B, C and crystal field parameters Dq, Ds and Dtwere calculated from the following equations:

$$^2B_{2g} \rightarrow ^2E_g \quad = \quad E_1 = -3Ds + 5Dt \qquad (1)$$

$$^2B_{2g} \rightarrow ^2B_{1g} = \quad E_2 = 10\,Dq \qquad (2)$$

$$^2B_{2g} \rightarrow ^2A_{1g} = \quad E_3 = 10\,Dq - 4Ds - 5\,Dt \qquad (3)$$

Inter-electronic repulsion parameters of VO^{2+} doped SnO_2 thin films referred to tetragonal field. By solving the above three equations the evaluated values are obtained as Dq = 1418, Ds = -2201 and

Dt = 1328 cm^{-1}. The observed values of VO^{2+} doped SnO_2 thin films are in good agreement with the calculated values. The energy bandgap transitions, inter-repulsion parameter values are presented in Table-1. The obtained results are in good agreement with Yadav et al.[64]

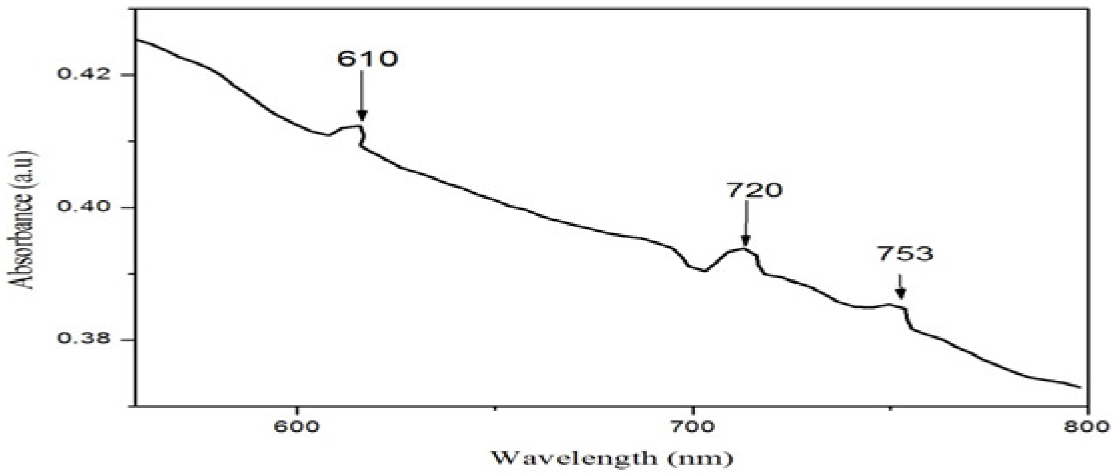

Fig.-1: Optical absorption spectrum of VO^{2+} doped SnO_2 thin films

Electrical Properties

The dc electrical conductivity measurements were performed on to VO^{2+} doped SnO_2 thin films by employing four probe setup. By varying the temperature (1000/T) with respect to log R, a plot has been observed with two linear parts as shown in Figure-2. The dc dielectric resistance can be measured by the following equation:

$$R= R_0 \exp (\Delta E / KT) \quad (4)$$

Where ΔE is the difference in temperature attributed in two activation processes; it can be described as: (1) intrinsic conduction band forms at high temperature region and (2) extrinsic conduction band forms at low temperature region. The conduction band is formed due to hopping of charge carriers localized at Fermi level. As the temperature is increases the charge carriers attributed which in turns increase of conductivity[65].

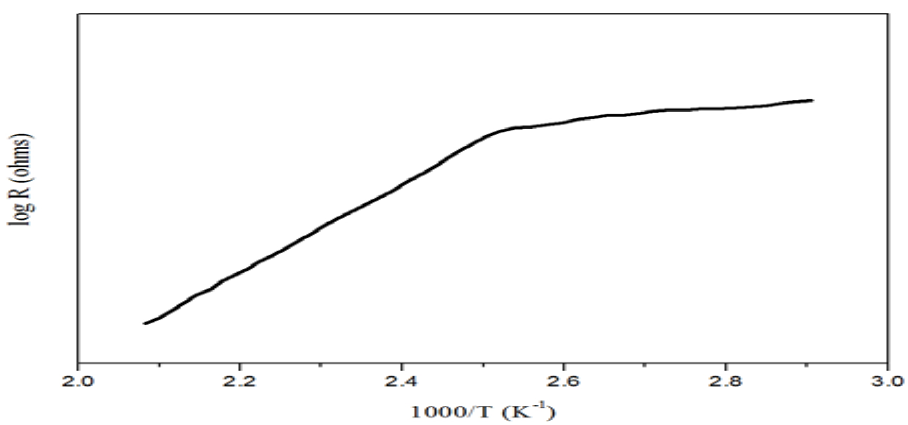

Fig. -2: Plot of log R versus 1000/T of VO^{2+} doped SnO_2 thin films

Thermo emf

Thermo emf can be measured by the variation of temperature with induced thermoelectric voltage across the material. The thermo emf of VO^{2+} doped SnO_2thin films was studied in the temperature range 275 - 325 K using thermal probe method. Thermo emf can be calculated by the following equitation:

$$S = - \Delta V/\Delta T \quad (5)$$

Where, S is the thermo power; ΔT is temperature difference between the two ends of a material and ΔV is thermoelectric voltage at the terminals.
Variation of thermo emf with respect to temperature difference of the thin film is found to be linear, which is clearly shown in Figure-3. The thermo emf of VO^{2+} doped SnO_2thin films increased with the increasing of temperature, whereas at low temperatures the Seebeck coefficient decreases predominantly with increasing of temperature[66]. This result shows that VO^{2+} doped SnO_2thin films are typical of semiconductor behaviour. The obtained results are in good agreement with Mohamma et al.[67]

Table-1: Optical band positions, crystal field and inter-electronic repulsion parameters of VO^{2+} doped SnO_2 thin films

Transition from $^2B_{2g}$ ↓	Wavelength (nm)	Wavenumber (cm^{-1})		Dq (cm^{-1})	Ds (cm^{-1})	Dt (cm^{-1})
		Observed	Calculated			
^2E_g	610	16,393	16,398	1418	-2201	1328
$^2B_{1g}$	720	13,889	13,878			
$^2A_{1g}$	753	13,280	13,286			

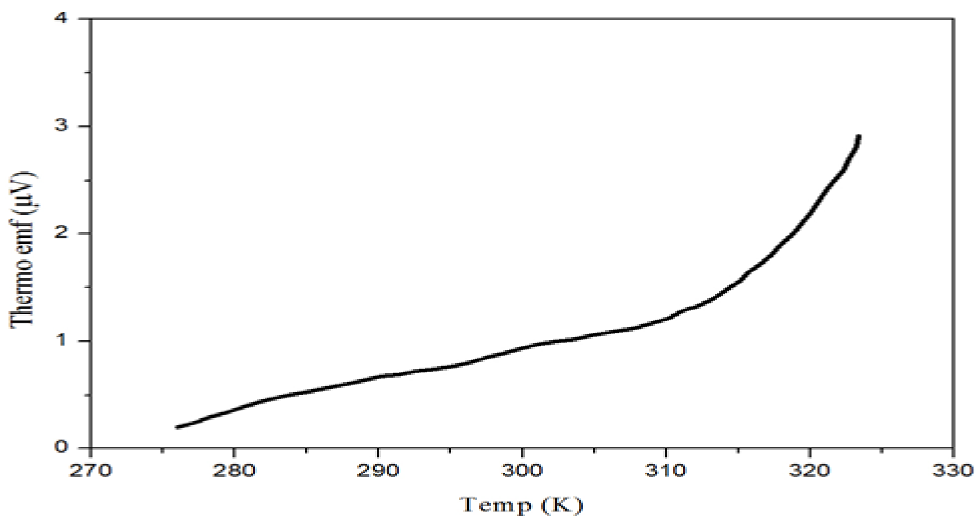

Fig.- 3: Temperature dependence of thermo emf on VO^{2+} doped SnO_2thin films

Photoluminescence Studies

Photoluminescence studies have been carried-out for the prepared thin film on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources.PL spectrum explores the information of dopant elements. Figure-4 shows PL spectrum of VO^{2+} doped SnO_2thin film consists of four bands at 352, 436 nm and the other bands at 462 and 578 nm in the visible region corresponding to blue and yellow regions respectively.
The UV emission; which is also known near band-edge emission (NBE) is observed in the spectrum due to high intensity and recombination of free excitons in collision process. The other band which is observed at 462 nm is possibly attributed to the electron transition mediated by defect levels in the bandgap, such as oxygen vacancies. In general the singly charged oxygen vacancy gives to green emission and doubly charged oxygen vacancies is commonly attributed to the yellow one (~ 580 nm)[68, 69]. In the present study the band observed at 578 nm is attributed to yellow region.
From luminescent properties, the CIE 1931 chromaticity coordinates are calculated for the prepared thin film and the chromaticity coordinates from the emission spectrum is found to be at x = 0.2993 and y = 0.4912. The corresponding CIE diagram is shown in Figure-5. The location of the color coordinates for VO^{2+} doped SnO_2 thin films in CIE chromaticity diagram is about in blue and yellow region.

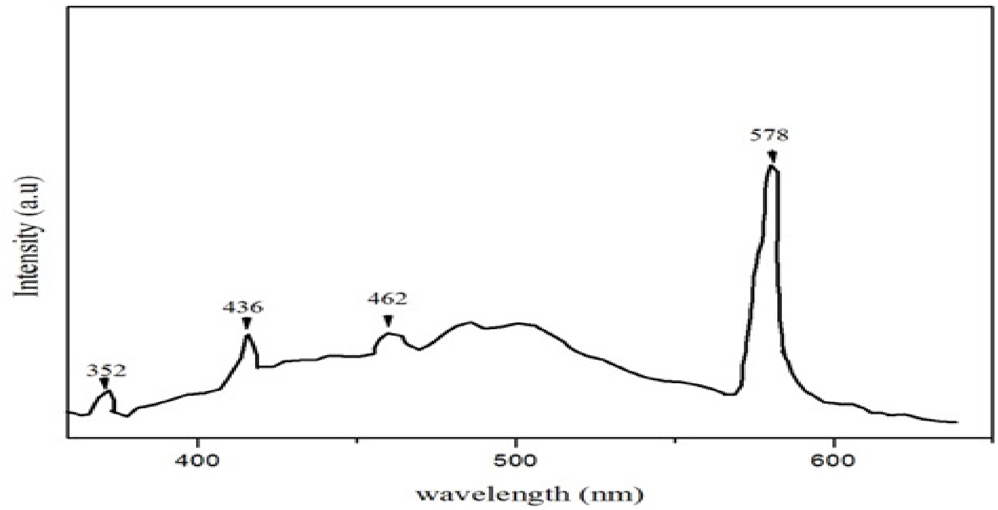

Fig.-4: PL spectrum of VO^{2+} doped SnO_2 thin films

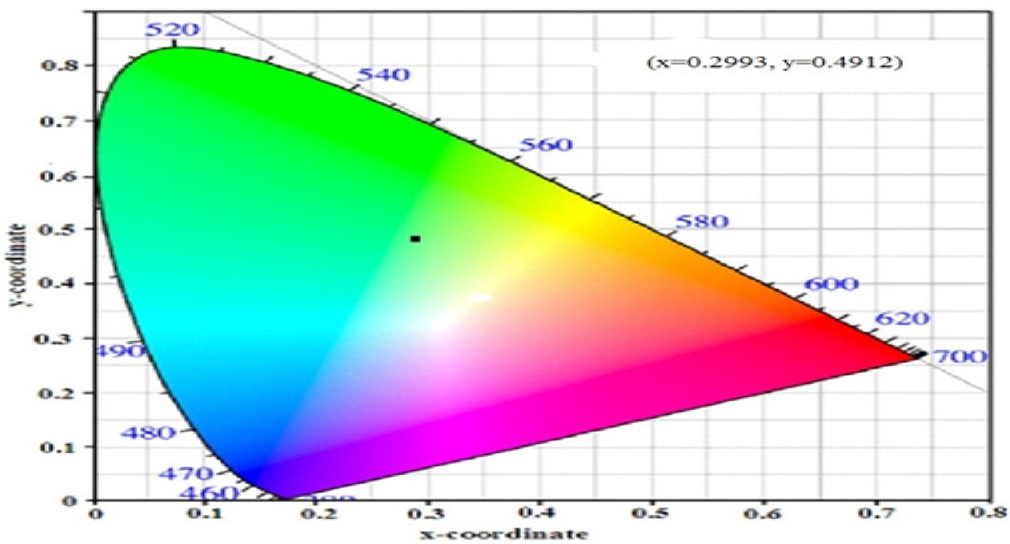

Fig.-5: CIE diagram of VO^{2+} doped SnO_2 thin films

CONCLUSION

VO^{2+} doped SnO_2 thin films were prepared by chemical spray pyrolysis technique. Optical absorption studies revealed that the vibration of molecules in energy levels from ground state to exited state which depends on the nature of the symmetry and the ligand complex. Electrical conductivity measured revealed that if the temperature increases then the charge carriers attributed which in turns increasing of conductivity. Thermo emf of VO^{2+} doped SnO_2thin films increased with the increasing of temperature. PL studies shows four characteristic bands which are formed due to octahedral site symmetry. The location of the color coordinates of VO^{2+} doped SnO_2 thin films in CIE chromaticity diagram is about in blue and yellow regions. Based on the obtained results, these materials may be used for LEDs, electroluminescence panels and plasma display devices.

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